

PATENT SPECIFICATION

(11) 1338 275

1338 275

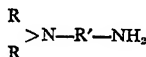
NO DRAWINGS

- (21) Application No. 26790/71 (22) Filed 19 April 1971
 (31) Convention Application No. 27134 (32) Filed 9 April 1970 in
 (33) United States of America (US)
 (44) Complete Specification published 21 Nov. 1973
 (51) International Classification C08G 22/44, 22/36
 (52) Index at acceptance
 C3R 32B1 32B2 32D6A 32E1 32E2 32G1 32H1 32H2 32J2Y
 (72) Inventors PETER FREDERIK JOSEPH GEIJSSEN and BO
 CHRISTER LOEFGREN



(54) A PROCESS FOR MAKING A POLYURETHANE FOAM

- (71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
 This invention concerns a process for making a polyurethane foam and more particularly relates to foamed polyurethanes made by the reaction of polyether polyols with organic polyisocyanates in the presence of a reactive amine catalyst. The use of tertiary amine catalysts in such reactions is well known.
 In its broadest aspect, the present invention resides in the use of a particular class of amine catalyst-reactants in the production of polyurethane foams. They are tertiary-primary polyamines which may be called dialkylamino-substituted primary amines, and are represented by the formula



- wherein each R independently is a lower alkyl group, i.e., having up to 6 carbon atoms, or the two may be joined together to make, with the nitrogen atom to which they are attached, a heterocyclic ring of 3 to 6 members, and R' is a divalent hydrocarbon radical preferably having 2—10 carbon atoms.
 Suitable amines having the above formula include the dialkylaminoalkylamines such as dimethylaminoethylamine, dibutylaminoethylamine, dihexylaminopropylamine, 2 - (N - methyl - N - propylamino) - 1 - butylamine and 4 - (dimethylamino) - 2 - hexylamine; the heterocyclic aminoalkylamines such as 2 - (1 - aziridinyl)ethylamine, 3 - (1 - pyrrolidinyl) - 1 - propylamine and 4 - (1 - piper-

idinyl) - 2 - hexylamine; aminoalkylpiperazines, such as N - (2 - aminoethyl) - piperazine, 1,4 - bis - (2 - aminoethyl) - piperazine and 1 - (4 - amino - 1 - butyl) - 2, - 6 - dimethylpiperazine and dialkylaminoarylamines, such as N,N - dimethyl - p - phenylenediamine, N,N - dibutyl - m - phenylenediamine and 4 - (N,N - diethylaminomethyl)aniline.

The above amines may be used in a wide range of proportions, depending on other processing variables, particularly the presence or absence of other catalysts. Ordinarily, improved results are obtained with 0.1 to 5%, by weight, of these amines, based on the polyol in the formulation, the preferred amount usually being 0.3 to 2%. They may be used in conjunction with other catalysts, such as triethylenediamine and tin salts.

The polyols and isocyanates useful with the above amines include all of those commonly used in making rigid or flexible foamed polyurethanes. Typical polyols include the polyether polyols made by condensing one or more alkylene oxides with a polyfunctional initiator such as water, glycol, glycerol, sorbitol, or sucrose. For making highly elastic flexible foams, the polyol should have an OH equivalent weight of 850—2500 and should include at least a substantial proportion of triol of molecular weight at least 3000 and at least 25%, and preferably at least 40%, of the hydroxyl content should be primary hydroxyl. Such high primary OH content is usually achieved by capping the polyol with 5—25% by weight of ethylene oxide, based on the total oxide content.

For making rigid or semi-rigid foams, polyols of lower molecular weight and/or higher functionality are ordinarily used, such as the polyether polyols of OH equivalent weight 80—1000 and functionality 3 to 8 or more.

The polyisocyanate used in conjunction with the above amines may be any of those normally used in making polyurethane foams. These include the tolylene diisocyanates, including the

[Price 25p]

so-called "crudes" which contain polymeric isocyanates of functionality greater than 2, the polyphenylene polyisocyanates, the chain-extended polyisocyanates and isocyanate-terminated prepolymers made by condensing an excess of a simpler polyisocyanate with a polyol, such as a glycol or polyglycol or a glycerol-initiated polyether triol. In the preferred embodiment of highly elastic flexible foams the preferred isocyanates are those having a functionality of more than 2, i.e., at least 2.1, and preferably 2.2 to 3.0.

In making foams containing the above amines, the usual additives, such as blowing agents, fillers, pigments, stabilizers and dyes can be included in the usual ways. However, when making the preferred highly elastic flexible foams, it is advantageous to avoid the use of silicone materials. While no surfactant is necessary for making such products, non-silicone surfactants, such as the aryl alkyl-sulfonates and the alkyl arylsulfonates, can often be used advantageously. For example, short-chain glycols, alkanolamines or aliphatic polyamines help stabilize such foams when used as a minor component of the polyol, as do non-silicone type stabilizers.

In a preferred embodiment of the invention, the amine catalyst-reactants of the invention are used in conjunction with polyether polyol of OH equivalent of at least 1000, polyisocyanate of functionality of at least 2.0, water, a fluorocarbon blowing agent, and in the absence of silicone surfactant, to produce highly elastic, low density, flexible foams. These are preferably made in a continuous slabstock bun or a cold-curing molding operation. Such product is essentially open-celled, has high modulus, improved hysteresis, improved resilience and rubber-like feel, and outstanding fire resistance. While the preponderant proportion of the polyol in such formulations is polyether polyol of OH equivalent at least 1000, it is sometimes advantageous to add a very minor proportion, of the order of 1 to 10%, by weight, of the total polyol of a short-chain diol, triol or aliphatic polyamine such as diethylene glycol, tripropylene glycol or tri-

ethanolamine. These help stabilize the foam during the foaming and curing stage.

The practice of the invention is illustrated by the following examples.

Examples 1—7.

A series of runs was made with a low-pressure foam machine operated at a through-put of 21—22 kg./min., conveyor speed of 2.2—2.6 m./min., air flow (60 p.s.i.g.) (5 atm) of 500—600 cc./min. and mixer speed of 2900—3200 r.p.m. Cream time was 7—10 sec. and rise time was 55—90 sec. The polyol was a commercial triol made by condensing propylene oxide with glycerol and then capping the product with ethylene oxide so that its final molecular weight is 4600 and the primary OH content is 45% (based on total OH).

The isocyanates are identified as follows:

- A. A crude tolylene diisocyanate (2,4 and 2,6 isomers and in addition some tri- and higher isocyanates; average functionality between 2 and 3).
- B. A 50:50 blend of distilled tolylenediisocyanate (80:20 2,4:2,6 isomers) with so-called "Crude MDI". MDI is methylene-diisocyanate, also known as diphenylmethanediisocyanate.

The catalysts are identified as follows:

- A. Triethylenediamine, 33% solution in di-propylene glycol.
- B. 3-dimethylamino-1-propylamine (DMAPA).

Other abbreviations used herein are:

DEG, diethylene glycol
PPS, phenyl pentadecylsulfonate

Table I shows the formulations used and the properties of the foams produced in typical examples of the present invention. In the table, all parts are by weight and are based on 100 parts of the polyol.

All the foams rated "Self-extinguishing" and had burning rates of 6.0 to 8.5 cm./min. (ASTM D—1692).

TABLE I
Preparation and Properties of Flexible Foams

Formulation	Example No.						
	1	2	3	4	5	6	7
Isocyanate	A	A	A	A	A	A	B
Isocyanate Index	80	100	105	105	105	105	105
Water	2.0	2.0	2.0	2.5	2.5	2.0	2.0
DEG	0	0	0	0	5	4	4
PFS	4.5	4.5	4.5	0	0	0	0
Cat. (p.p.s.)	B(0.5)	B(0.5)	$\begin{Bmatrix} A(0.5) \\ B(1.0) \end{Bmatrix}$	$\begin{Bmatrix} A(0.5) \\ B(0.5) \end{Bmatrix}$	$\begin{Bmatrix} A(0.5) \\ B(0.5) \end{Bmatrix}$	$\begin{Bmatrix} A(0.5) \\ B(1.0) \end{Bmatrix}$	$\begin{Bmatrix} A(0.5) \\ B(1.0) \end{Bmatrix}$
Properties*							
Density, Kg./m. ³	65	44	49	34	36	48	48
Tensile Str., Kg./cm. ²	0.35	0.45	1.25	0.70	1.00	1.25	0.85
Elongation, %	240	200	160	145	130	170	130
Tear Str., Kg./cm.	0.25	0.30	0.45	0.30	0.30	0.45	0.28
Resilience, %DB (ASTM)	65	62	66	60	56	65	65
90% Compression Set, %	90	90	90	90	75	90	7.0
Hysteresis, %	17	19	15	20	21	15	14
40% CLD, g./cm. ³	6.2	11	22	15.5	18.5	20	22

* According to DIN where not otherwise stated.

Example 8—12.

In a second series of experiments, hand-mixed batches of material were poured and foamed and the foams were tested as in the previous examples.

- 5 In each example, the polyol was made by condensing propylene oxide with glycerol until a molecular weight of about 4000 was reached and then condensing the intermediate with 5
10 moles of ethylene oxide per OH equivalent in the intermediate.

The isocyanate used was that designated "B" in the previous examples and was used in an amount corresponding to an isocyanate index of 105.

Each formulation included 3.5 parts of water and 7 parts of triethanolamine per 100 parts of polyol. Other components (parts per 100 parts of polyol) are indicated in Table II, as are the properties of the resulting foams.

Cream times were 6—9 seconds while rise times were 70—120 seconds.

TABLE II

Formulation, Parts per 100 parts polyol	Example No.				
	8	9	10	11	12
Fluorotrichloromethane				5	10
Dimethylaminopropylamine	1.00			1.00	1.20
Diethylaminoethylamine		1.25			
N-(2-Aminoethyl)aziridine			1.50		
Properties					
Density, Kg./m. ³	32.8	31.2	35.0	29.2	26.0
Tensile Str., Kg./cm. ²	.45	.45	.50	.40	.40
Elongation, %	75	60	55	80	80
Tear Str., Kg./cm.	.30	.35	.29	.28	.26
Resilience, % DB (ASTM)	57	57	54	56	54
90% Compression Set, %	7.5	11.5	11.0	9.0	12.0
Hysteresis, %	23	26	25	23	25
40% CLD, g./cm. ²	23.5	24	31	20	15

- 25 To illustrate the utility of the novel catalysts in the production of rigid foams, the following experiments were conducted.

Examples 13—18.

- 30 In each of these examples, 100 parts of polyol were used, the polyol being that obtained by condensing propylene oxide with a mixture of sucrose and glycerol (approximately 1:3 molar ratio) until the product has a hydroxyl number of 490.

The isocyanate used contained 40% diisocyanate, the remainder being tri- and higher functionality. It was used in an amount corresponding to an isocyanate index of 105.

The formulations also included 45 parts of fluorotrichloromethane and 2 parts of a silicone-glycol surfactant.

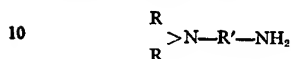
The amine catalyst-reactant, reaction characteristics and density of the resulting foams are shown in Table III.

TABLE III

Formulation	Example No.					
Amine, parts	13	14	15	16	17	18
Dimethylaminopropylamine	1.5	2.0	2.5			
N(2-Aminoethyl)aziridine				1.0	2.0	3.0
Reaction Characteristics						
Cream time, sec.	30	27	22	55	40	} Not measured
Rise time, sec.	210	150	135	380	240	
Tack-free Time, sec.	330	190	150	720	330	
Density of Foam						
Kg./m. ³	25	25	26	25.5	26	26

WHAT WE CLAIM IS:—

- 5 1. A process for making a polyurethane foam which process comprises mixing and reacting a polyisocyanate with a polyetherpolyol in the presence of a polyamine catalyst and a blowing agent wherein the reaction is carried out in the presence of a catalytic proportion of a polyamine of the formula



- 15 wherein each R independently is a 1 to 6 carbon alkyl group or the two may be joined with the nitrogen to form a heterocyclic ring of 3 to 6 members and R' is a divalent hydrocarbon radical.

2. A process as claimed in claim 1 wherein R' is a divalent hydrocarbon radical having from 2 to 10 carbon atoms.

- 20 3. A process as claimed in claim 1 or claim 2 wherein the polyamine employed is a dialkylaminoalkylamine, a heterocyclic aminoalkylamine, an aminoalkylpiperazine or a dialkylaminoarylamine.

- 25 4. A process as claimed in any one claims 1 to 3 wherein the polyisocyanate employed has an average functionality of at least 2.1.

5. A process as claimed in any one of the preceding claims wherein the polyisocyanate

employed has an average functionality of from 2.2 to 3.0.

6. A process as claimed in any one of claims 1 to 5 wherein the polyether polyol employed has an average hydroxyl equivalent weight of 850 to 2500.

7. A process as claimed in claim 6 wherein at least 25 per cent of the hydroxyl groups of the polyol employed are primary hydroxyl groups.

8. A process as claimed in claim 6 wherein at least 40 per cent of the hydroxyl groups of the polyol employed are primary hydroxyl groups.

9. A process as claimed in any one of the preceding claims wherein the polyamine catalyst is employed in an amount of from 0.1 to 5 per cent by weight based on the weight of the polyol.

10. A process as claimed in any one of the preceding claims wherein the polyamine catalyst is employed in an amount of from 0.3 to 2 per cent by weight based on the weight of the polyol.

11. A process for making a polyurethane foam substantially as hereinbefore described in any one of the specific examples.

12. A polyurethane foam whenever obtained by a process as claimed in any one of claims 1 to 11.

30

35

40

45

50

55

BOULT, WADE & TENNANT,
Chartered Patent Agents,
112 Hatton Garden, London, EC1N 8NA.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.